BIODEGRADABLE POLYMERIC FLOCCULANTS BASED ON CASSAVA STARCH GRAFTED WITH POLYDIALLYLDIMETHYLAMMONIUM CHLORIDE

by

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LIST OF ABBREVIATIONS

Abbreviation	Description
ac	Alternating Current
AGU	Anhydrous Glucose Unit
ANOVA	Analysis of Variance
CCD	Central Composite Design
DADMAC	Diallyldimethylammonium Chloride
dc	Direct Current
DF	Degree of Freedom
DoE	Design of Experimental
EDX	Energy-dispersive X-ray spectroscopy
FAU	Formazin Attenuation Unit
FI	Flocculation Index
FTIR	Fourier Transform Infra-Red Spectroscopy
GPC	Gel Permeation Chromatography
HES	Hydroxyethyl Starch
HPLC	High Performance Liquid Chromatography
KPS	Potassium Persulfate
Mn	Number Average Molecular Weight
Mw	Weight Average Molecular Weight
MWD	Molecular Weight Distribution
Mz	Z-average Molecular Weight
NA	Not Available

NMR	Nuclear Magnetic Resonance
NTU	Nephelometric Turbidity Unit
PAA	Polyacrylic Acid
PAM	Polyacrylamide
PDA	Photometric Dispersion Analyser
PDI	Polydispersity Index
PolyDADMAC	Polydiallyldimethylammonium Chloride
PPM	Part per Million
rms	Root Mean Square
rpm	Rotation per Minute
RSM	Response Surface Methadology
SEM	Scanning Electron Microscope
SLS	Static Light Scattering
TOC	Total Organic Carbon
TSS	Total Suspended Solid
XRD	X-ray Powder Diffraction

LIST OF SYMBOLS

Symbol	Description
%	Percentage
°C	Degree Celsius
mg/L	Milligram per Litre
mV	Millivolts
cm^{-1}	Reciprocal Centimetres
kDa	Kilo Dalton
V	Volt
µm	Micrometer
g/mol	Gram per Mole
Y	Response (dependent variable),
b_0	Constant Coefficient
b_i	Coefficient for The Linear Effect
b_{ii}	Coefficient for The Quadratic Effect
b_{ij}	Coefficient for The Interaction Effect
ε	Experimental Error
p	Probabilities
F	Mean Square for Lack of Fit to the Mean Square for Pure Error
R^2	Proportion of Variation
dL/g	Deciliters per gram

Δ	Delta
D_1	Floc Ratio Before Breakage
D_2	Floc Ratio After Breakage
D_3	Floc Ratio in Re-Steady State Region
X_1	Mole Ratio of DADMAC to Starch (AGU)
X_2	Reaction Temperature
X_3	Initiator Concentration
X_4	Reaction Time
N	Total experiment
n	Total Variables
g	gram
mL	Millilitre
$wt\%$	Weight per cent
mm	Millimetre
λ	Wavelength
$Å$	Angstrom
Wi	Initial Weight of The Sample
Wr	Weight After Taken Out
dm^3	Cubic Decimetre
T_1	Turbidity or TSS samples After Been Treated
T_0	Initial of Turbidity or TSS Samples
Y	Response
α	Alpha

POLIMER PENGGUMPAL TERBIODEGRADASI BERASASKAN KANJI UBI KAYU TERCANGKUK DENGAN POLIDIALLILDIMETILAMMONIUM KLORIDA

ABSTRAK

Kerja penyelidikan ini telah dilakukan untuk meneroka penyediaan dan mengoptima proses pencangkukan, kelakuan penggumpalan dan kriteria pengaggregatan emping oleh kanji ubi kayu tercangkuk polidiallyldimethilammonium klorida (polyDADMAC). Proses optimum ditentukan dengan kaedah gerak balas permukaan (response surface method, RSM) yang terdiri daripada tiga peringkat dan empat pemboleh ubah berbentuk komposit pusat. Keadaan optimum yang diperolehi adalah 1.96 (nisbah mol DADMAC kepada kanji), 40°C (suhu tindak balas) 0.09 mol/L (kepekatan pemula) dan 4.99 jam (masa tindak balas). Hasil eksperimen sebenar adalah 21.98% pada keadaan yang optimum, yang mana hampir dengan nilai maksimum yang diramalkan iaitu 22.80%. Selepas itu, keupayaan degradasi sampel dicangkukan telah diselidik dengan menggunakan kaedah penanaman tanah. Didapati bahawa peratusan cangkukan yang lebih tinggi menunjukkan penurunan berat yang lebih tinggi berbanding dengan sampel-sampel cangkuk yang lain dan kanji asli. Keupayaan degradasi itu disahkan dengan menganalisa kumpulan berfungsi mereka, berat molekul dan morfologi sampel. Keberkesanan penggumpalan bagi sampel yang dicangkukkan telah diselidik di dalam kaolin terampai. Keberkesanaan adalah berdasarkan penyingkiran kekeruhan dan jumlah pepejal terampai (total suspended solid,TSS). Ia menunjukkan bahawa mekanisme bagi sampel dicangkukan adalah peneutralan caj dan perapatan di mana ianya berlaku serentak. Ia juga didapati bahawa penyingkiran bertambah baik dengan peningkatan peratusan cangkuk.

Kelakuan penggumpalan dikaji lebih mendalam dengan memerhatikan pengagregatan, kerosakan dan pertumbuhan semula emping dengan menggunakan penganalisis penyebaran photometrik (photometric dispersion analyser, PDA). Pembesaran emping meningkat dengan peningkatan peratusan cangkuk kerana peningkatan keupayaan dan partikel-partikel telah dinyah-stabilkan. Ia juga mendedahkan peningkatan ricihan dan masa akan mengurangkan faktor kekuatan dan pemulihan bagi emping-emping.

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ABSTRACT

This research work was conducted to explore the preparation and optimization of grafting process, flocculation behaviour and flocs aggregation characteristic of cassava starch grafted with polydiallyldimethylammonium chloride (polyDADMAC). The optimization process was achieved by using response surface methodology (RSM) comprising three-levels and four-variables central composite design. The optimum condition derived were 1.96 (mole ratio of DADMAC to starch), 40°C (reaction temperature), 0.09 mol/L (initiator concentration) and 4.99 hour (reaction time). The actual experimental yield was 21.98% at optimum conditions, which was close to the maximum predicted value of 22.80%. Subsequently, the biodegradability of grafted samples was investigated by using soil burial method. It was found that higher grafting percentage shows higher weight loss compared to other grafted sample and native starch. The biodegradability was confirmed by analysis their functional groups, molecular weight and morphology of the samples. The effectiveness flocculation of grafted samples was investigated in kaolin suspension. The effectives were based on turbidity and total suspended solid (TSS) removal. It was shown that mechanism for grafted samples are charge neutralization and bridging which occurred concurrently. It was also found that removal was improved with increasing of grafting percentage. The flocculation behaviour was further studied in details by observing the aggregation, breakage and regrowth of flocs using photometric dispersion analyser (PDA). The flocs growth

increase with increasing of grafting percentage because of the improvement of interaction between grafted flocculants and suspended. It was reveal the increased of the shear and time will reduce the strength and recovery factor of flocs.

CHAPTER 1

INTRODUCTION

1.1 Research background

The demand of water steadily increased with the population of humans. This trending enhanced water scarcity phenomenon. Water scarcity phenomenon occurred when the water demand exceeding the available of water supplies (Gleick and Ajami, 2014). The problems become more severe when the water pollution spread to the freshwater supply. Most developing countries including Malaysia faced this problem with the major cause is that, the wastewater from industries are not treated before disposing it into rivers (Ujang and Buckley, 2002). According to Lee et al. (2014), the wastewater usually consists of dissolved solids, very fine suspended solids, inorganic and organic particles, metals and also other impurities.

Flocculation is one of the way and cost effective solution to the water treatment problems, especially in the case of suspended particles which cannot be filtered and spontaneously 'settle' down by itself. It is a process where dispersed particles are bridged together to form bigger flocs which will settled and cause clarification of the water system (Sharma et al., 2006). Flocculants are classified into two categories, inorganic and organics. Inorganic flocculants mostly used in wastewater treatment are multivalent metals based such as aluminium and ferum (Khalek and Mahmoud, 2011). However, there are several disadvantages using this metal based flocculants. It requires a large volume of dosage, very sensitive to pH changes and cannot be used in the system with very fine dispersed particles.

There are polymeric based which are used as an organic flocculants. This type of flocculants can be divided into two groups which are natural and synthetic. Synthetic polymeric flocculants have been largely used in wastewater treatment, particularly those containing suspended colloidal particles (Lin et al., 2012, Pandey et al., 2014). These flocculants exhibit high efficiency in particle removal, but several flocculants generate "secondary pollution" in the environment (Xie et al., 2007, Xing et al., 2010). Synthetic flocculants and their derivatives pose a number of environmental problems because some of the derivatives are non-biodegradable and the intermediate products of their degradation are hazardous to human health (Ho et al., 2010).

To address this issue, several researchers preferred natural polymers or known as green flocculants such as starch and chitosan (Teh et al., 2014, Yang et al., 2014a). Natural polymers are biodegradable, cheap, and fairly shear stable, but their shelf life depends on their biodegradability (Tripathy and Singh, 2000). Their biodegradability reduces their shelf life. For these reasons, green flocculants with high efficiency removal have attracted attention of researchers. Green flocculants (natural polymer) with high efficiency removal (synthetic polymer) can be achieved by combining these two types of polymeric flocculants.

1.2 Problems statement

Recently, many efforts have been made to produce green flocculants such as starch to solve the environmental issue poses by synthetic polymeric flocculants. Natural polymers are biodegradable, cheap, and fairly shear stable, but their shelf life